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OPTICAL STUDIES OF NATURAL DYES AND GREEN SYNTHESIZED SILVER NANOPARTICLES EMBEDDED IN TITANIUM (IV) OXIDE FOR APPLICATION IN DYE SENSITIZED SOLAR CELLS

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Abstract

Solar energy is unlimited in quantity and is becoming one of the most promising alternative sources of energy. DSSC is a new organic-based energy conversion device with simple fabrication procedures. This research focuses on the optical characteristics of natural dyes and green synthesized silver nanoparticles incorporated into TiO₂ for application in DSSCs. Natural dyes were extracted from air-dried neem (*Azadirachta indica*) and henna (*Lawsonia inermis*) leaves. The fresh henna leaf extract was prepared and added to AgNO₃ solution to synthesize silver nanoparticles. The TiO₂ pastes were prepared and deposited on glass substrates as thin films by doctor blade technique, dried and annealed at 450 °C. The TiO₂ film samples were soaked in dye solutions for sensitization and characterized using UV-Vis Avantes spectrophotometer. The ethanolic neem and henna dye extracts showed intense Soret and Q absorption bands at the visible range of the electromagnetic spectrum. The optical absorption band obtained at about 425 nm confirmed the presence of the AgNPs. Incorporating the silver nanoparticles into the TiO₂ increased the absorbance and the absorbance increased significantly in the wavelength region from 425 to 700 nm after loading with dye and inversely proportional to the energy gap. From this research, the natural dyes and green synthesized silver nanoparticles optical properties are shown to be good materials for the application in DSSCs with outstanding performance.

Keywords: Solar energy, Dye sensitized solar cell, TiO₂, Silver nanoparticles, *Azadirachta indica*, *Lawsonia inermis*

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Introduction

DSSC is a class of organic-based photovoltaics with tremendous potential that could serve as a replacement for silicon-based solar cells. Nevertheless, DSSC is not yet commercially marketed because it cannot match the conversion efficiency of energy in silicon-based devices, which is about 25% (Green *et al.*, 2012). The original DSSC efficiency was reported to be 7% (O'regan and Gratzel,

1991) and since then improved to 11% (Gratzel, 2005). An understanding of the fundamental mechanisms of DSSCs and identification of the processes that hinder their efficiency would lead to the fabrication of better DSSCs which are commercially viable.

DSSC is merited with being flexible, relatively high power conversion efficiency, low usage of toxic chemicals and simple fabrication procedures. DSSC

comprises of a photo-anode and a counter electrode with an electrolyte sandwiched in between. TiO₂ coated with a transparent conducting glass is used as the photo-anode. Dye is used as sensitizer and, when exposed to light, electrons are generated, injected into the TiO₂ layer and electricity is produced.

DSSC was first fabricated by Gratzel and coworkers (Green *et al.*, 2012). Significant improvements, however, have been made by other scientists in the design and preparation of its components for improvement of the efficiency of DSSCs (Kojima *et al.*, 2009). Among the components of a DSSC, the sensitizer is the major component which has an enhanced efficiency with its ability to absorb photons at the visible range of the electromagnetic region.

Early DSSC fabrications involved ruthenium-based dyes as sensitizers because of their effectiveness (O'Regan and Grätzel, 1991; Grätzel, 2005; Ito *et al.*, 2008). However, there is need for the use of cheaper, simpler, and safer dyes as alternatives due to high cost and undesired environmental impact of ruthenium-based dyes. Natural dyes offer suitable alternatives to high cost inorganic based DSSCs. The fruit, flowers and plant leaves display different colours and include different natural dyes which can be easily extracted for DSSC fabrication. Natural pigments are promising alternative sensitizers for DSSC because of their simple extraction technique, availability, complete biodegradation, affordability, purity, environmental friendliness, high reduction of noble metal and cost of chemical synthesis (Adedokun *et al.*, 2016).

Natural pigments, such as chlorophyll, carotene and anthocyanin are available freely in the photosynthetic plant leaves, flowers and fruits and they fulfill all these requirements. Porphyrin is an organic

group of chemical compounds which has intense light absorption at the visible region within the spectra. Due to the crucial role of chlorophyll (an example of porphyrin) in photosynthesis, its huge diversity and controllable electrochemical properties make it a prospective candidate for DSSC production. Experiments have shown that natural-dye sensitized TiO₂ solar cells have made an improvement in efficiency up to 7.1% with high stability (Campbell *et al.*, 2007).

Plasmon resonance concept has been currently adopted in the fabrication of DSSC (Ishikawa *et al.*, 2004). This is employed to a greater extent to improve the efficiency of DSSC. It intensifies the electromagnetic field near the surface of metal nanoparticles, resulting in the plasmon enhanced light absorption by dye sensitizers in DSSC. Recently, plasmonic effect of silver nanoparticles has been revealed as a prospective approach to maintain an efficient trapping of light in solar cells (Liu *et al.*, 2010).

In this study, natural dyes were extracted from air-dried neem (*Azadirachta indica*) and henna (*Lawsonia inermis*) leaves. The henna leaf broth extract was prepared and added to AgNO₃ solution to produce silver nanoparticles. TiO₂ pastes were prepared and deposited on glass substrates as thin films by doctor blade technique. The coated substrates were dried and annealed at 450 °C. The samples were soaked in the dye solutions for sensitization. The optical characterizations were accomplished using UV-Vis spectrophotometer.

Materials and Methods

The substrates were cleaned using detergent solution for 10 to 15 min and ultrasonically rinsed in water bath distilled water for 15 min at 30 °C. The substrates were later cleaned with IPA in ultrasonic bath for 15 min at 30 °C and were blow-dried in nitrogen environment.

Fresh Neem (*Azadirachta indica*) and Henna (*Lawsonia inermis*) leaves were collected, washed with distilled water and air dried. The dried leaves were ground into powders separately and kept safe. Each of the powders was weighed (10 g) and poured into clean bottles. Absolute ethanol (100 ml) was added to each sample and stirred with glass rods until uniform suspensions were obtained. The solutions were left in the dark for 24 h to guarantee a complete extraction. They were then filtered using Whatman filter paper No 1 to remove solid fragments and the dye extracts were kept in other clean bottles and protected from sunlight to ensure stability before use.

The fresh leaves extract of henna was prepared with 20 g of thoroughly washed leaves in 200 ml sterile distilled water in a clean beaker, boiled for 30 min and also filtered. The filtered extract was kept in a refrigerator at low temperature for stability. The quantity of the leaf extract was varied to 0.1, 0.2, 0.3 and 0.4 ml with the same silver nitrate (50 ml of 1 mM of AgNO_3) solution to synthesize silver nanoparticles. That was done to ensure optimization of extract concentration needed to synthesize silver nanoparticles. The TiO_2 paste was prepared by mixing 1 g of the powder with 10 ml of ethanol and heated at 90 °C under stirring for 1 h to obtain a homogeneous solution. Ethanol was chosen as a solvent because it has no characteristic absorption and emission at the visible region.

Also, the green synthesized AgNPs were mixed with the same volume (1 ml) of TiO_2 paste in different volume (ml) of 0.2, 0.4 and 0.6 for the purpose of optimization. Then, 0.5 cm by 0.5 cm border was made by means of Scotch Magic tape on the glass substrates. The obtained pastes were deposited on glass substrates as thin films by doctor blade technique. Also, a reference electrode was prepared without AgNPs. Assuming

uniformity, the thickness of the TiO_2 thin film was determined by equation 1. The film thickness was approximately equal to 16.67 μm .

$$t = \frac{M_2 - M_1}{2AD} \quad (1)$$

M_1 = Mass of substrate alone

M_2 = Mass of substrate and film

A = surface area of the film

D = Density of TiO_2 film (3.895 g/cm^3)

For stability of the films, the coated slides were preheated, then annealed at 450 °C for 30 min in a furnace and allowed to cool down to room temperature. They were then kept in well covered substrate rack to prevent contamination. Each of the TiO_2 coated specimens was soaked in the dye extract solutions with the semiconductor coated surface facing up and left for 18 h for sensitization. Then, specimens were removed, air-dried and kept in sealed petridishes. The outer surfaces of the dishes were protected with aluminium foil to prevent the specimens from direct sunlight. The band gap energy E_g and absorption coefficient (α), are related by the equation (2).

$$(ah\nu)^2 = h\nu - E_g \quad (2)$$

Where $h\nu$ is the incident photon energy.

Results and Discussion

Optical Absorbance of Dyes

The UV-Vis optical absorptions of ethanol dye extracts of *Azadirachta indica* and *Lawsonia inermis* are shown in Figure 1. The colours of the extracted natural dyes are shown in Figure 2 (A and B). It is observed that the major intense absorption peaks of the natural dyes as shown in Figure 1 are centered mainly on wavelengths 415 nm and 665 nm respectively. The dye extracts showed intense absorption in the region of 350-500 nm and 630-700 nm indicating the presence of chlorophyll. The intense Soret and Q bands observed, and weak bands

shown in the spectral range between them are in conformity with the corresponding

literature data shown for Pheophytin 'a' (Adedokun *et al.*, 2018).

Figure 1: UV-Vis optical absorption of *Azadirachta indica* and *Lawsonia inermis* dye extracts

Figure 2: Extracted natural dyes. A: Neem dye extract; B: Henna dye extract

Optical Absorbance of Silver Nanoparticles

Figure 3 shows the formation of silver nanoparticles. As the henna leaf extract and the aqueous solution of the silver ion complex were mixed together, the colour changed from colourless to grey. The major constituents of henna is red-orange dye known as lawsone and it also have gallic acid as one of its constituents (Khare, 2007). The silver nanoparticle is grey in colour when gallic acid is used for

its synthesis. From this, it may be deduced that gallic acid is employed by the henna as a reducing agent. There was a blue shift due to surface plasmon resonance of silver nanoparticles as the concentration of leaf extract increased. This might also be due to increase in reduction potential of the leaf extract which leads to more reduction of silver nitrate into silver nanoparticles. As concentration of leaf extract increased, the rate of the reaction also increased, as shown in Figure 4.

Figure 3: Formation of AgNPs. A: Silver nitrate, B: Plant extract, C: Silver nanoparticles

Figure 4: AgNPs formed at different concentrations of fresh Henna leaf extract (A: 0.1 ml, B: 0.2 ml, C: 0.3 ml, D: 0.4 ml in 50 ml of 1 mM of Silver nitrate)

The optical absorption for silver nanoparticles with varying concentrations of *Lawsonia inermis* leaf extract as reducing agent is shown in Figure 5. Silver nanoparticles were synthesized at different concentrations of leaf extract and analyzed by UV spectra. Plasmon resonance band observed at about 425 nm is similar to those reported work in the literature (Obaid *et al.*, 2015). As the concentration of extract was increased, there was higher absorption intensity. The UV-Vis spectra recorded implied that most rapid bio-

reduction was achieved using *Lawsonia inermis* leaf extract as a reducing agent. The UV-Vis spectra and visual observation revealed that silver nanoparticles formation happened rapidly within few minutes.

Optical Absorbance of TiO₂ Film Samples with Dyes

The UV-Vis optical absorptions of TiO₂ film samples with and without dyes are displayed in Figure 6. The TiO₂

nanoparticles without dye did not show any absorbance at the visible region because of a wide band gap. The absorbance increased at the visible region of the electromagnetic spectrum after loading of dyes.

Optical absorbance of TiO₂ film samples with silver nanoparticles

The UV-Vis optical absorption of TiO₂ film samples with silver nanoparticles is shown in Figure 7. As stated earlier, the TiO₂ nanoparticles without dye has no absorbance at the visible region because of its wide band gap. Incorporating the silver nanoparticles into it influenced the absorbance at the visible region due to the surface plasmon resonance nature of the silver nanoparticles.

Optical absorbance of TiO₂ film samples with AgNPs and dyes

The UV-Vis optical absorptions of TiO₂ film samples with silver nanoparticles and dyes are displayed in Figure 8 and 9 respectively. The results show that the absorbance significantly increased at the visible region after loading of dyes. It shows that the silver nanoparticles sufficiently enhanced the absorption by the dyes. This signifies increase in the efficiency of the solar cell. The enhancement of the absorbance varies with the silver nanoparticles concentration as the UV-Vis spectrum of TiO₂ mixed with 0.6 ml silver nanoparticles showed a wider absorption than those of the other TiO₂ layers.

Figure 5: UV-Vis optical absorption of the silver nanoparticles synthesized with *Lawsonia inermis* leaf extract

Figure 6: UV-Vis optical absorption of TiO_2 film samples with and without natural dyes

Figure 7: UV-Vis optical absorption of TiO_2 Film samples with silver nanoparticles synthesized with Henna leaf extract

Figure 8: UV-Vis optical absorption of TiO_2 film samples with silver nanoparticles and Neem dye

Figure 9: UV-Vis optical absorption of TiO_2 film samples with silver nanoparticles and Henna dye

Optical band gaps

The optical band gaps calculations for the films were estimated from the curves of $(\alpha h\nu)^2$ versus $h\nu$. The energy band gaps were obtained from straight line plot of $(\alpha h\nu)^2$ versus $h\nu$ by extrapolating the line to the base line, as displayed in Figures 10 and 11 for the TiO_2 loaded with Neem dye extract and TiO_2 loaded with Henna dye extract.

From the results, as shown in Tables 1 and 2, it implies that energy gap decreases with an

increase in absorbance. Reduction in the energy gap increases the conductivity of the material since the electrons will require less energy to travel the Fermi level of the material (Ito *et al.*, 2007). When the photon hits the dye molecule, electron will be excited and jump from the HOMO to LUMO state. After reaching the LUMO state, the electron will be conveyed to the conduction band of the TiO_2 electrode. Therefore, reduction in the energy gap of the paste will result in better transportation of electron to the TiO_2 conduction band.

Figure 10: Optical band gaps for the TiO_2 film and TiO_2 film samples loaded with AgNPs and Neem dye

Figure 11: Optical band gaps for the TiO_2 film and TiO_2 film samples loaded with AgNPs and Henna dye

Table 1: Optical band gap for the TiO_2 film samples loaded with Neem dye

Sample	Energy Gap (eV)
TiO_2 thin film	3.80
TiO_2 thin film loaded with Neem dye	3.65
TiO_2 thin film incorporated with 0.2ml AgNPs and loaded with Neem dye	3.60
TiO_2 thin film incorporated with 0.4ml AgNPs and loaded with Neem dye	3.55
TiO_2 thin film incorporated with 0.6ml AgNPs and loaded with Neem dye	3.40

Table 2: Optical band gap for the TiO_2 film samples loaded with Henna dye

Sample	Energy Gap (eV)
TiO_2 thin film	3.80
TiO_2 thin film loaded with Henna dye.	3.75
TiO_2 thin film incorporated with 0.2ml AgNPs and loaded with Henna dye	3.49
TiO_2 thin film incorporated with 0.4ml AgNPs and loaded with Henna dye	3.26
TiO_2 thin film incorporated with 0.6ml AgNPs and loaded with Henna dye	2.99

Conclusion

Natural dyes from *Azadirachta indica* and *Lawsonia inermis* were prepared and characterized. The UV-Vis absorption properties of the extracted dyes show absorption peaks identical to the Pheophytin 'a'. AgNPs was synthesized and the optical absorption band obtained at about 425 nm confirmed the formation of the AgNPs. AgNPs was incorporated into TiO₂ and the absorbance increased at the visible region. After dye loading, the absorbance significantly increased at the visible region. The energy gap was noticed to be decreasing as the absorbance increases. The results of this research has shown that optical properties of natural dyes and green prepared silver nanoparticles using *Azadirachta indica* and *Lawsonia inermis* are good materials for dye sensitized solar cells applications.

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References

- Adedokun, O., Awodele, M.K., Sanusi, Y.K. and Awodugba, A.O. 2018. Natural dye extracts from fruit peels as sensitizer in ZnO based dye-sensitized solar cells. *IOP Conference Ser.: Earth Environmental Science* 173: 012040.
- Adedokun, O., Titilope, K. and Awodugba, A.O. 2016. Review on natural dye-sensitized solar cells (DSSCs). *International Journal of Engineering Technologies* 2(2): 34-41.
- Campbell, W.M., Jolley, K.W., Wagner, P., Wagner, K., Walsh, P.J., Gordon, K.C., Schmidt-Mende, L., Nazeeruddin, M.K., Wang, Q., Grätzel, M. and Officer, D.L. 2007. Highly efficient porphyrin sensitizers for dye-sensitized solar cells. *Journal of Physical Chemistry C* 111(32): 11760-11762.
- Gratzel, M. 2005. Solar energy conversion by Dye-sensitized photovoltaic cells. *Inorganic Chemistry* 44(20): 6841-6851.
- Green, M.A., Emery, K., Hishikawa, Y., Warta, W.D. and Dunlop, E.D. 2012. Solar cell efficiency tables (Version 39). *Progress in Photovoltaics* 20(1): 12-20.
- Ishikawa, K., Wen, C.J., Yamada, K. and Okubo, T. 2004. The photocurrent of dye sensitized solar cells enhanced by the surface plasmon resonance. *Journal of Chemical Engineering Japan* 37(5): 645-649.
- Ito, S., Chen, P., Comte, P., Nazeeruddin, M. K., Liska, P., Pechy, P. and Grätzel M. 2007. Fabrication of screen-printing pastes from TiO₂ powders for dye-sensitized solar cells. *Progress in Photovoltaics: Research and Applications* 15(7): 603-612.
- Ito, S., Murakami, T.N., Comte, P., Liska, P., Grätzel, C., Nazeeruddin, M.K. and Grätzel, M. 2008. Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%. *Thin Solid Films* 516(14): 4613-4619.
- Khare, C.P. 2007. Indian medicinal plants – An illustrated dictionary, Springer, New York.
- Kiruba Daniel, S.C.G., Nehru K. and Sivakumar M. 2011. Rapid biosynthesis of silver nanoparticles using *Eichornia crassipes* and its antibacterial activity. *Current Nanoscience* 8(1): 125-129.
- Kojima, A., Teshima, K., Shirai, Y. and Miyasaka, T. 2009. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of American Chemical Society* 131(17): 6050-6051.
- Liu B., Liu F., Chen C. and Gao H. 2010. Supercritical carbon dioxide extraction of ethyl P-methoxycinnamate from *Kaempferia galanga* L. rhizome and its apoptotic induction in human HepG₂ cells. *Natural Product Research* 24: 1927-1932.
- O'Regan, B. and Gratzel, M. 1991. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* 353: 737-740.